Emission Characteristics of AC-operated Electrochemiluminescent (ECL) Cell with Electroconductive Polymer

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Electrochemiluminescence (ECL) is known as electrochemical reaction exhibiting emission, and is applicable to new imaging device. We have been studying the Emission characteristics of ECL cell containing a Ruthenium(II) complex as luminescent species. The emission turn-on response time and emission intensity were dramatically improved by introducing AC method.

In this paper, we studied the phenomena of ECL cell with electroconductive polymer like as poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) instead of a Ruthenium (II) complex. Orange light emitted from the ECL cell of MEH-PPV with a turn-on voltage of AC 4V at 10Hz for the first time.

Keyword: Luminescence, ECL, OLED, Ruthenium, Conductive Polymer, poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene];(MEH-PPV), Electrochromic reaction

1. Introduction

Nowadays, flat panel displays such as liquid crystal display (LCD), plasma display panel (PDP), and organic light emitting diode (OLED) are growing in popularity.

In small size display such as tablet PC and smart Phone, OLED display is very popular and familiar because of their thin shape, light weight, emissive mode display.

However, OLED have difficulty in fabrication for large-area devices because vacuum evaporation processes are commonly required to prepare such devices. Further, during the vacuum evaporation process, organic materials were vacuum-evaporated by heating. This heating process sometimes results in deformation of molecular structure and reaction between molecules. These limit the variety of applicable organic molecules.

Therefore, new emitting devices that can be fabricated by simple process such as coating process or printing process are required for mass production, especially in large-area devices [1,2].

ECL is a well known light emission phenomenon by electrochemical reaction and its emission occurs from excited state formed by collision of cation radical and anion radical generated at cathode and anode, respectively [3].

ECL devices are driven by direct current (DC) and alternate current (AC) method. The response time of emission at common DC method is slow. (approximately a second).

This is because the emission occurs after diffusion of cation and anion radical generated from opposite electrodes. In AC-driven ECL (AC-ECL), both cation and anion radical are generated from one electrode due to repeated change of electrode polarity. AC-ECL improves the
turn-on response by colliding with cation radical at near the one electrode (around millisecond time scale) \[4\].

ECL is well-known luminescence phenomenon of organic molecules that is based on oxidation reduction \[3\]. Many studies have been conducted on the use of ECL for light sources and display device \[3,5,6\]. There is no requirement for using low work function metals. Also there is no need barrier film.

Electroconductive polymer are currently attracting great interest for use in various applications, e.g., field-effect transistor\[7,8,9\], solar cells\[10,11,12\], data-storage devices \[13,14,15\], and the polymer-based light-emitting diodes\[16,17,18,19,20\].

In this paper, ECL cell with MEH-PPV film by AC driven was successfully demonstrated for the first time. We describe the electrochemical operating mechanism of ECL cell with MEH-PPV.

### 2. Experimental

#### 2.1. Materials

Poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV) was used as an emitting material (Aldrich, Mn = 70,000-100,000) was used as an emitting material. Tetra-n-butylammoniumhexafluoro-phosphate (TAPF6) was used as supporting electrolyte in polymeric gel. Propylene carbonate (PC) was used as solvent (For Electrochemistry-Grade, Kanto Chemical Co., Ltd.). Tetra-butyl ammonium perchlorate (TBAP) as supporting electrolyte (Cica-Reagent, Kanto Chemical Co.). ITO electrodes were purchased from Sanyo Vacuum Industries Co., Ltd.

MEH-PPV were dissolved in pyridine (MEH-PPV solution). ITO glass substrates were cleaned by subsequent ultrasonic treatment in detergent, acetone, and isopropyl alcohol.

The MEH-PPV film was obtained directly on the adequately washed ITO glass electrode by cast coating from the MEH-PPV solution, which resulted in conjugated polymer films with a thickness of about 2 micron. The films were dried at 353 K for 8 h in vacuo.

#### 2.2. Measurement

Cyclic voltammetry (CV) measurements were carried out with a electrochemical analyzer (ALS/CH Instruments Model 440A).

AC Voltage was applied to ECL cells with a function generator (IWATSU SG-4105).

The ECLs were measured with a photonic multichannel analyzer(Hamatsu PMA C 10027). Absorption spectra were recorded in situ during the DC voltage applying using Ocean Optics USB2000 diode array detection system.

### 3. Results and Discussion

#### 3.1. MEH-PPV film on ITO substrate with gel electrolyte.

Figure 1 shows the cross-section of ECL cell. 100mM of TAPF6 and 10 wt% of PMMA were dissolved in acetonitrile, which was a gel electrolyte. This gel electrolyte was on MEH-PPV film on ITO glass substrate.

**Figure 1. Schematic showing the cross-sectional view of planar device**

**Figure 2. Cyclic voltammogram of the MEH-PPV ECL cell**

Figure 2 depicts the electrochemical characteristics of ECL devices probed by cyclic voltammetry (CV). The CV of MEH-PPV cell was measured by scanning of potential from 2.5V to -2.5V (versus Ag/AgCl).

Figure 3 shows cyclic voltammograms (bottom) and absorbance of MEH-PPV (top) scanning of potential from 2.5V to-2.5V (versus Ag/AgCl).

When the 1.5 V was applied, MEH-PPV film changed its color from orange to black by oxidation reaction. In case of at 0V, Its
absorption decreased. This means that MEH-PPV (oxidant) returned to be neutral state. Absorbance value increase over +1.5V. It means electrochromic reaction.

MEH-PPV at CV. This result supported that the emission was not observed from this device.

Because ECL shows a well-known light emission phenomenon by electrochemical reaction, its emission occurs from excited state formed by collision of cation radical (oxidant) and anion radical (reductant) generated at cathode and anode.

3.2. Double face MEH-PPV on ITO/glass with gel electrolyte

We developed new following device. Figure 5 shows the cross-section of double face ECL cell.

![Figure 3 Change in absorbance (up) and cyclic voltammogram (down) of the MEH-PPV ECL cell.](image)

![Figure 4. Cyclic voltammogram of the MEH-PPV ECL cell at 1st cycle(top) and 2nd cycle(bottom)](image)

Figure 4 shows cyclic voltammogram of the MEH-PPV ECL cell at scanning 1st time and 2nd time. There were no any peak from 0V to -1.5V at the first scanning, but there was some peak at the second scanning. This means that the oxidant of MEH-PPV became at first scanning returned to be neutral state. There was no reduction reaction of MEH-PPV.

Figure 5. Schematic showing the cross-sectional view of planar device

![Figure 6. Change in absorbance(top) and cyclic voltammogram(bottom) of the ECL cell.](image)

Figure 6 shows cyclic voltammograms (bottom) and absorbance of MEH-PPV (top) scanning of potential from 2.5V to 2.5V (versus Ag/AgCl). When +2.5V was applied, MEH-PPV film on working electrode was oxidized. On the other hand, MEH-PPV on reference electrode was deoxidized. Then CV current value increased. The current peaks at +/-0.2V were ascribed to be neutral state from oxidant and reductant. We confirmed that there were oxidation-reduction reaction on same electrode.

This result suggests that MEH-PPV cell will evolve ECL phenomenon by AC driven. We never obtained any emission from this ECL...
device under the application of AC 3 V at 50 Hz. We thought that current value was too small for ECL under the application of AC 3V at 50 Hz.

3.3 Duble face MEH-PPV on ITO/glass with electrolyte solution.

Figure 7 shows the cross-section of new ECL cell. We exchanged electrolyte with electrolyte from gel electrolyte as follow.

![Figure 7. Schematic showing the cross-sectionnal view of planar device](image)

Figure 8. shows cyclic voltammograms of MEH-PPV ECL cell scanning of potential from 2.5V to-2.5V (versus Ag/AgCl). This ECL cell thickness was controlled at 300 μm by a film spacer. The CV results was same as Figure 6. But the current value of Figure 8. were more than Figure 6. This result indicates the MEH-PPV ECL is active in an electrochemical reaction.

![Figure 8. Cyclic voltammogram and photo of ECL cell.](image)

And MEH-PPV film changed color form orange (neutral state) to black (oxidant) as from orange to black as pictures in Figure 8.

The ECL spectrum obtained from the device under the application of AC 4V, at 10Hz is shown in Figure 9. The ECL cell emitted orange luminescence. The emission peak was at 620 nm. The ECL bands with an emission maximum at 620 nm was almost identical to photo-luminescence (PL) of MEH-PPV, indicating that the light was emitted from the MEH PPV.

![Figure 9. Electrochemiluminescent spectra of ECL cell containing MEH PPV under AC 4V at 10 Hz (top) and Digital camera image of an emitting ECL cell (bottom).](image)

The effect of applied frequency on the emission intensity for the ECL cell was studied. The results were plotted as a function...
of frequency is Figure 10. As can been seen is Figure 3, the intensity of emission became higher as the frequency decreased.

4. Conclusion

In this paper, We successfully demonstrated an AC-driven ECL cell with electroconductive polymer like as MEH-PPV for the first time. The emitted luminance was increasing by going down frequency. We expect that the results of this research will contribute to the development of novel display device such as digital signage and E-paper.

References